

VII.F.3 Selective Catalytic Oxidation of Hydrogen Sulfide

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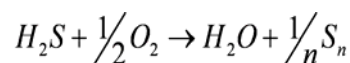
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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop and optimize low-cost carbon-based catalysts for the selective oxidation process to reduce sulfur levels to the parts-per-billion (ppb) range in an H₂-rich gas stream in order to produce a low- to zero-sulfur fuel for use in fuel cells. The main reaction is represented by the following equation:



- Identify activated carbon catalysts that show potential for complete conversion of H₂S without formation of undesired products.
- Investigate different activation protocols and carbon-based precursors that can lead to improved catalytic properties, and design catalysts with optimum properties.
- Perform catalytic studies of catalysts in H₂-rich streams and model reformat gas streams to determine catalytic activity, selectivity, durability, and regeneration processes.
- Investigate reaction mechanisms and pathways for byproduct formation, such as carbonyl sulfide (COS) and sulfur dioxide (SO₂).
- Investigate reaction conditions that lead to complete and exclusive conversion of H₂S to elemental hydrogen and elemental sulfur.
- Characterize the microstructures, surface properties, and impurity levels of the catalysts and correlate them to catalytic activity, selectivity, and durability.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- I. Hydrogen Purification/Carbon Monoxide Cleanup—Reduction of emission of toxic chemicals derived from the presence of sulfur compounds in the fuel.

Technical Targets

The project is conducting fundamental studies in the development of carbon-based catalysts that can reduce sulfur levels to the ppb range in a H₂-rich gas stream. The lab-made catalysts have demonstrated the capability to reduce sulfur levels of fuel gas streams to less than 200 ppb without formation of byproducts such as COS and SO₂.

Approach

- Investigate different sources of carbon and activation processes that can lead to carbon-based materials with improved activity and selectivity for the H₂S removal reaction.
- Characterize the catalysts and correlate the effects of pore volume, pore size and distribution, impurities, surface functional groups, and catalyst morphology to catalytic performance.
- Investigate the effect of reaction conditions on the activity and selectivity.
- Investigate reaction mechanisms and the formation of byproducts in H₂-rich streams containing variable amounts of other compounds such as water vapor and carbon monoxide.

Accomplishments

- Synthesized activated carbons that displayed superior activity and selectivity as catalysts for H₂S oxidation. The synthesized catalysts are capable of converting H₂S exclusively to elemental sulfur and H₂ in both H₂ and simulated reformat streams.
- Characterized surface morphology, surface area and pore size distribution, surface functionalities, and impurity composition of several commercial and laboratory-synthesized activated carbons.
- Evaluated the effect of temperature, O₂/H₂S ratio, and space velocity on the activity and selectivity.
- Conducted catalytic tests for monitoring catalyst behavior in a shorter time at a relatively high H₂S concentration and in several gas streams containing variable amounts of CO, CO₂, and H₂O to evaluate formation of byproducts.
- Demonstrated the capability of lab-made catalysts to reduce sulfur levels of fuel gas streams to less than 200 ppb without formation of byproducts such as COS and SO₂.

Future Direction

- Design catalysts based on optimization of the synthesis process. Synthetic carbon catalysts should be produced with controlled structure, morphology, and impurity content that can lead to enhanced catalytic properties.
- Investigate durability and regeneration processes.
- Develop a systematic study to understand the importance of the impurity contribution to reaction and evaluate the roles and significance of surface functional groups.

Introduction

Hydrogen is commonly produced by reforming of natural gas; however, reformat contains impurities, such as H₂S, that can poison shift catalysts and fuel cell electrodes. In fuel cell applications, even a low concentration (a few ppm) of hydrogen sulfide can dramatically shorten the life of fuel cell catalysts. Therefore, the removal of sulfur-containing compounds from H₂-rich fuels is very important. Selective catalytic oxidation of H₂S using an activated carbon catalyst is a highly promising method for the removal of H₂S from fuel cell hydrocarbon feedstock [1]. The primary objective of this project is to develop a carbon-based

catalyst that promotes oxidation of H₂S to elemental sulfur, reducing sulfur contamination to the ppb range or better in H₂-rich fuel streams.

Although the use of activated carbons for selective oxidation of H₂S to elemental sulfur has been suggested as a preferred approach for removal of sulfur from gas streams, the key mechanisms for H₂S removal and the critical features in an activated carbon catalyst are not well understood. Additionally, one of the main difficulties with the use of this technology is the formation of byproducts such as SO₂ and COS. This project is focused on the design and fundamental investigation of the catalytic properties of low-cost, carbon-based catalysts that

can successfully reduce the sulfur level in fuel cell feedstocks to meet the desired level.

Approach

The research is geared toward a fundamental understanding of the catalytic properties of the carbon catalyst that will enable the design of catalytic materials that can continuously remove H₂S to the ppb range in H₂-rich fuel streams. For this purpose, an integrated effort is required that includes optimization of synthesis of carbon-based materials, structural and chemical characterization, and finally reaction studies.

The carbon materials were synthesized; and the effects of the precursor material, heat treatment, and activation process were evaluated. Activation was achieved by exposing the carbon precursor to an oxidizing gas (CO₂ or steam) for varying lengths of time in order to produce materials with variable microstructures. Different precursors were used to produce carbon catalysts with varying impurity levels. The performance of all carbon materials synthesized and obtained commercially was measured and compared in a fixed-bed reactor equipped with a gas chromatograph and an infra-red detection system. The effect of operational parameters was tested by varying the temperature, O₂/H₂S ratio, and space velocity. The formation of byproducts such as SO₂ and COS was investigated under varying gas compositions.

The characterization of the materials' properties is being carried out to identify the surface microstructures, functionalities, and impurity contents and their relationships with the synthesis protocol and the performance of carbon catalysts. Inorganic impurities [2] and surface functional groups [3] have been shown to play an important role in the catalytic activity of the carbon-based materials. The impurities were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) screening and inductively coupled plasma optical emission spectroscopy (ICP-OES), and highly pure carbons were synthesized to isolate their effects. Another important aspect to be addressed is the kind of pore structure and the pore size distribution desired for an active, selective, and durable catalyst. Nitrogen adsorption isotherms (Bruner, Emmett and Teller

surface area analysis method, BET) analysis and density functional theory calculations were performed to determine the surface area and pore size distribution of the catalysts. Thermogravimetric analysis and the Boehm titration method [4] are being applied to investigate the chemical nature of the carbon surface. Studies concerning the relationship between the activation burn-off level of activated carbons, the pore size distribution, and catalytic behavior have been conducted. Long-term reactivity tests are being used to evaluate the durability of the catalysts and regeneration processes. The lab-made catalysts are being independently tested for the removal of sulfur in coal streams through a partnership with the National Energy Technology Laboratory. Industry applications and partnering are under discussion with United Technologies, ConocoPhillips, and Chevron.

Results

We have developed an improved activated carbon catalyst that can selectively oxidize H₂S in H₂-rich gas streams without consumption of H₂. Our lab-made catalysts have demonstrated the capability for continuous removal of sulfur to less than 200 ppb levels. Figure 1 illustrates the differences among the lab-made catalyst and several commercial catalysts tested using a model reformat stream containing 1000 ppm of H₂S in 50% H₂, 15% CO₂, 9% CO, 2% CH₄, and 23% H₂O. The conversion of H₂S and sulfur yield were calculated using these equations:

$$\text{Conversion of } H_2S (\%) = \frac{C_{H_2S,in} - C_{H_2S,out}}{C_{H_2S,in}} \times 100;$$

$$\text{Selectivity to sulfur } (\%) = \frac{C_{H_2S,in} - C_{H_2S,out} - C_{COS,out} - C_{SO_2,out}}{C_{H_2S,in} - C_{H_2S,out}} \times 100$$

It is clear from Figure 1 that the undesired formation of gaseous sulfur byproducts such as SO₂ and COS is a key aspect for the successful performance of the lab-made catalysts, and it is the main problem for the commercial carbon materials.

Besides the catalyst properties, the operational conditions must be optimized in order to achieve high conversion and selectivity. The effects of temperature, O₂/H₂S ratio, and space velocity were

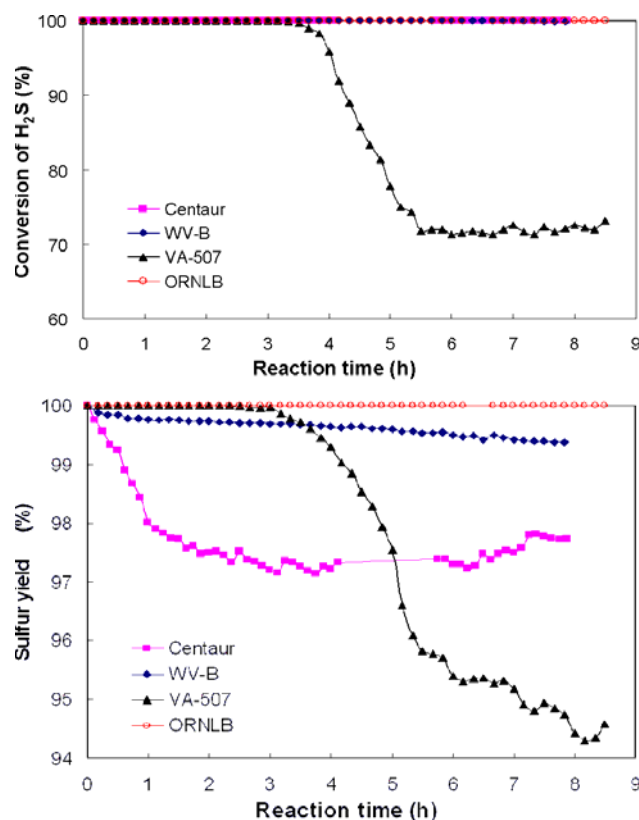
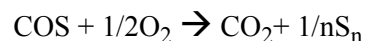


Figure 1. Comparison of the elective catalytic oxidation activity (a) and selectivity (b) of 1000 ppm of H₂S in simulated reformat at T=150°C, O₂:H₂S=2:1, SV=3100 h⁻¹ of three commercial catalysts (Centaur, WV-B, and VA-507) and a lab-made catalyst.

investigated. Our studies showed that the activity and selectivity of activated carbons are strongly dependent upon the test conditions and the gas components. For instance, Figure 2 shows the influence of the O₂/H₂S ratio on the catalytic behavior of activated carbons in an H₂ stream at 150°C. It can be observed that a higher O₂/H₂S ratio results in a higher emission of SO₂ but does not significantly shift the SO₂ breakthrough time. In a reformat stream (Figure 3), an increase of the O₂/H₂S ratio suppressed the formation of COS, but the effect was not significant for ratios higher than 2:1.

The formation of byproducts was studied by varying the gas composition. Figure 4 shows the measured H₂S conversion and COS emission when a lab-made catalyst was tested using different gas

streams. It was found that the formation of byproducts such as COS is strongly dependent on the reactive mixture and that different reaction routes might be responsible for the changes in selectivity observed during this study. The most significant result from this effort is that our lab-made catalyst demonstrated a unique capability to partially oxidize COS as



The surface area, impurity content, and carbon structure of several commercial and lab-made

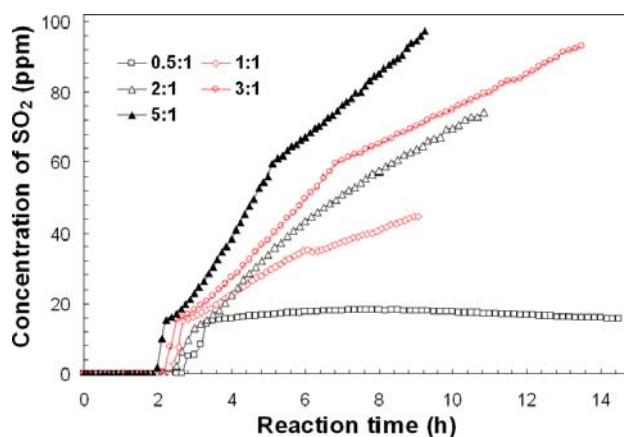


Figure 2. Effect of O₂:H₂S ratio on the catalytic behavior of a commercial activated carbon in H₂ stream containing 1000 ppm of H₂S at 150°C.

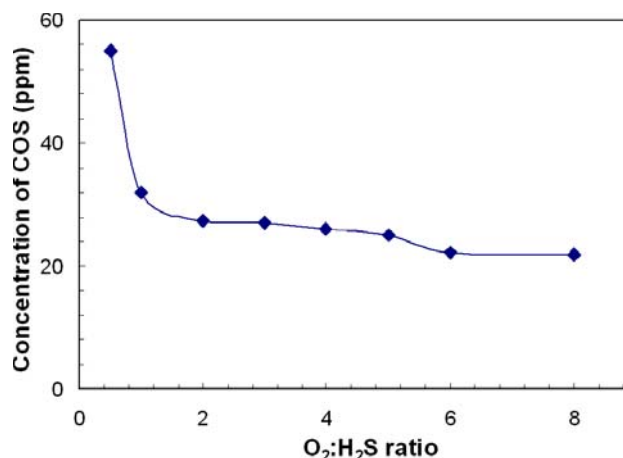


Figure 3. Effect of O₂:H₂S ratio on the emission of COS on a commercial activated carbon in reformat gas stream containing 1000 ppm of H₂S at 150°C.

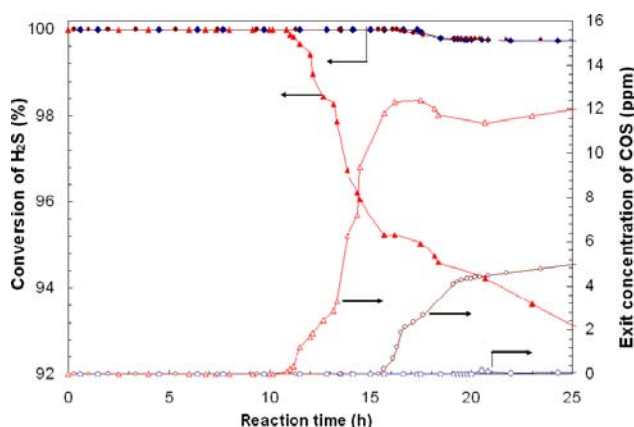


Figure 4. Conversion of H_2S and COS emissions in the presence of a lab-made catalyst: \blacklozenge in H_2 stream, \blacktriangle in reformate, \circ in dry reformate.

carbons are being studied and compared. The porosity and surface area are determined by BET analysis. The pore size distribution derived from density functional theory analysis reveals that all pores are smaller than 50 Å for the commercial catalysts, whereas a significant volume is in pores smaller than 10 Å in the case of the catalysts synthesized by Oak Ridge National Laboratory (ORNL). The impurity contents are identified and quantified by inductive coupled plasma analysis. Impurities such as phosphorous, sodium, calcium, potassium, and iron have been identified as major components in these catalysts. The surface acid-base properties are characterized using titration techniques, and results indicate that the commercial catalysts have more acidic surface sites than the ORNL catalysts.

Conclusions

- Activated carbons are inexpensive and can be used to remove sulfur to ppb levels from H_2 -rich gas streams. Several activated carbon materials have been synthesized and tested for the selective catalytic oxidation of H_2S .
- The process operates at low temperatures, and the ORNL-synthesized activated carbon demonstrated good activity and high selectivity toward H_2S oxidation, whereas side reactions are a problem for commercial activated carbons.

- The conversion and selectivity of H_2S are strongly dependent on operational conditions. Increased conversion can be achieved using a higher $\text{O}_2/\text{H}_2\text{S}$ ratio, lower space velocities, and higher temperatures. However, these factors show little effect on achieving exclusive conversion to elemental sulfur.
- The emission of byproducts such as COS and SO_2 seems to be dependent upon the sulfur vapor pressure level. The microstructures of the lab-made catalyst may be responsible for the build-up of sulfur in its micropores before the sulfur vapor pressure becomes high enough to form byproducts. Additionally, the lab-made carbon catalysts demonstrated a unique capability to partially oxidize COS.
- Many factors, such as impurities, microporosity, and surface functional groups may contribute to the differences in activity and are under investigation.

FY 2005 Publications/Presentations/Patents

- Xianxian Wu, Andrew K. Kercher, Timothy R. Armstrong, Viviane Schwartz, and Steven H. Overbury, "Activated Carbons for the Selective Catalytic Oxidation of Hydrogen Sulfide to Sulfur," *Carbon* 43, 1084 (2005).
- Xianxian Wu, Andrew K. Kercher, Viviane Schwartz, Steven H. Overbury, and Timothy R. Armstrong, "Activated Carbon as Catalyst for Removing Hydrogen Sulfide: On The Formation of By-Products," presented at the 2005 American Chemical Society meeting, San Diego, CA.
- Viviane Schwartz, Xianxian Wu, Andrew K. Kercher, Steven H. Overbury, and Timothy R. Armstrong, "Catalytic Properties of Activated Carbons for the Selective Oxidation of Hydrogen Sulfide," poster presented at the 19th North American Catalysis Meeting, Philadelphia, PA, 2005.

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